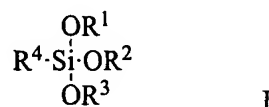


We claim:

1. A method of preparing siliceous materials comprising combining an organic polyol silane precursor with an additive under conditions suitable for the hydrolysis and condensation of the precursor to a siliceous material, wherein the additive is selected from the group consisting of one or more water-soluble polymers and one or more trifunctional silanes of Formula I:



wherein R¹, R² and R³ are the same or different and represent a group that may be hydrolyzed under normal sol-gel conditions to provide Si-OH groups; and R⁴ is group that is not hydrolyzed under normal sol-gel conditions.

2. The method according to claim 1, wherein the additive is a water soluble polymer is selected from the group consisting of polyethers, polyalcohols, polysaccharides, poly(vinyl pyridine), polyacids, polyacrylamides and polyallylamine.

3. The method according to claim 2, wherein the additive is a water soluble polymer is selected from the group consisting of polyethylene oxide (PEO), polyethylene glycol (PEG), amino-terminated polyethylene glycol (PEG-NH₂), polypropylene glycol (PPG), polypropylene oxide (PPO), polypropylene glycol bis(2-amino-propyl ether) (PPG-NH₂), polyvinyl alcohol, poly(acrylic acid), poly(vinyl pyridine), poly(N-isopropylacrylamide) (polyNIPAM) and polyallylamine (PAM).

4. The method according to claim 3, wherein the additive is a water soluble polymer is selected from the group consisting of PEO, PEO-NH₂, PEG, PPG-NH₂, polyNIPAM and PAM.

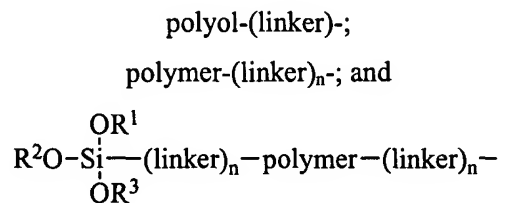
5. The method according to claim 3, wherein the additive is a water soluble polymer is selected from the group consisting of PEO, PEO-NH₂ and polyNIPAM.
6. The method according to claim 1, wherein the additive is a mixture of water soluble polymers,
7. The method according to claim 6 wherein the mixture of water soluble polymers comprises PEO and PEO-NH₂.
8. The method according to claim 5, wherein the additive is PEO.
9. The method according to claim 8, wherein the PEO has a molecular weight that is greater than about 10,000 g/mol.
10. The method according to claim 9, wherein the PEO is used at a concentration of greater than about 0.005 g/mL of final solution.
11. The method according to claim 5, wherein the additive is PEO-NH₂.
12. The method according to claim 11, wherein the PEO-NH₂ has a molecular weight that is greater than about 3,000 g/mol and is used at a concentration of about 0.005 g/mL of final solution.
13. The method according to claim 5, wherein the water soluble polymer is poly(*N*-isopropylacrylamide).
14. The method according to claim 13, wherein the poly(*N*-isopropylacrylamide) has a molecular weight that is about 10,000 g/mol and is used at a concentration of about 0.005 g/mL of final solution.

15. The method according to claim 1 wherein the one or more additives is a compound of Formula I.
16. The method according to claim 15, wherein OR^1 , OR^2 and OR^3 are the same or different and are derived from organic mono-, di-, or polyols.
17. The method according to claim 16, wherein OR^1 , OR^2 and OR^3 are the same or different and are derived from sugar alcohols, sugar acids, saccharides, oligosaccharides and polysaccharides.
18. The method according to claim 17, wherein OR^1 , OR^2 and OR^3 are the same or different and are derived from allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose, threose, erythrose, glyceraldehydes, sorbose, fructose, dextrose, levulose, sorbitol, sucrose, maltose, cellobiose, lactose, dextran, (500-50,000 MW), amylose, pectin, glycerol, propylene glycol and trimethylene glycol.
19. The method according to claim 18, wherein OR^1 , OR^2 and OR^3 are the same or different and are derived from glycerol, sorbitol, maltose, trehalose, glucose, sucrose, amylose, pectin, lactose, fructose, dextrose and dextran.
20. The method according to claim 18, wherein OR^1 , OR^2 and OR^3 are the same or different and are derived from glycerol, sorbitol, maltose and dextran.
21. The method according to claim 15, wherein OR^1 , OR^2 and OR^3 are the same or different and are selected from C_{1-4} alkoxy, aryloxy and arylalkyleneoxy.
22. The method according to claim 21, wherein wherein OR^1 , OR^2 and OR^3 are the same or different and are selected from C_{1-4} alkoxy, phenoxy, naphthyloxy and benzyloxy.

23. The method according to claim 22, wherein wherein OR¹, OR² and OR³ are the same or different and are selected from C₁₋₄alkoxy.

24. The method according to claim 23, wherein OR¹, OR² and OR³ are all ethoxy.

25. The method according to claim 15, wherein R⁴ is selected from one of the following groups:



wherein n is 0-1.

26. The method according to claim 25, wherein the polyol is an organic mono-, di-, or polyol.

27. The method according to claim 26, wherein the polyol is selected from the group consisting of a sugar alcohol, sugar acid, saccharide, oligosaccharide and polysaccharide.

28. The method according to claim 27, wherein the polyol is a selected from the group consisting of allose, altrose, glucose, mannose, gulose, idose, galactose, talose, ribose, arabinose, xylose, lyxose, threose, erythrose, glyceraldehydes, sorbose, fructose, dextrose, levulose, sorbitol, sucrose, maltose, cellobiose, lactose. dextran, (500-50,000 MW), amylose, pectin, glycerol, propylene glycol and trimethylene glycol.

29. The method according to claim 28, wherein the polyol is selected from the group consisting of glycerol, sorbitol, maltose, trehalose, glucose, sucrose, amylose, pectin, lactose, fructose, dextrose and dextran.
30. The method according to claim 29, wherein the polyol is selected from the group consisting of glycerol, sorbitol, maltose and dextrose.
31. The method according to claim 25 wherein the polymer is a water soluble polymer.
32. The method according to claim 31, wherein the polymer is selected from the group consisting of polyethylene oxide (PEO), polyethylene glycol (PEG), amino-terminated polyethylene glycol (PEG-NH₂), polypropylene glycol (PPG), polypropylene oxide (PPO), polypropylene glycol bis(2-amino-propyl ether) (PPG-NH₂), polyvinyl alcohol, poly(acrylic acid), poly(vinyl pyridine), poly(N-isopropylacrylamide) (polyNIPAM) and polyallylamine (PAM).
33. The method according to claim 32, wherein the water soluble polymer is selected from the group consisting of PEO, PEO-NH₂, PEG, PPG-NH₂, polyNIPAM and PAM.
34. The method according to claim 33, wherein the polymer is PEO.
35. The method according to claim 25, wherein the linker is selected from the group consisting of C₁₋₂₀alkylene, C₁₋₂₀alkenylene, organic ethers, thioethers, amines, esters, amides, urethanes, carbonates and ureas.
36. The method according to claim 25, wherein the compound of Formula I is selected from the group consisting of:
GluconamideSi (Compound 1);

MaltonamideSi (Compound 2);

DextronamideSi (Compound 3);

$(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 4-5$, average MW 200 (Compound 5a);

$(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 13$, average MW 600 (Compound 5b);

$(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 44$, average MW 2000 (Compound 5c); and

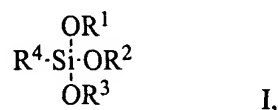
$(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 227$, average MW 10,000 (Compound 5d).

37. The method according to claim 1, wherein the organic polyol silane precursor is selected from the group consisting of diglycerylsilane (DGS), monosorbitylsilane (MSS), monomaltosylsilane (MMS), dimaltosylsilane (DMS) and a dextran-based silane (DS).

38. The method according to claim 1, wherein the conditions suitable for the hydrolysis and condensation of the precursor to a siliceous material include a pH in the range of about 4-11.5 in aqueous solutions and with optional sonication to assist in dissolution.

39. A method of preparing siliceous materials with low shrinkage characteristics comprising:

(a) combining an aqueous solution of one or more compounds of Formula I:



wherein R^1 , R^2 and R^3 are the same or different and represent a group that may be hydrolyzed under normal sol-gel conditions to provide Si-OH groups; and R^4 is group that is not hydrolyzed under normal sol-gel conditions with an aqueous solution of an organic polyol silane precursor;

(b) adjusting the pH of the solution in (a) to about 4-11.5;

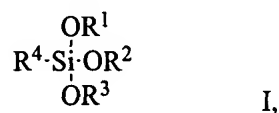
(c) allowing the solution of (b) to gel;

(d) aging the gel of (c); and

(e) drying the aged gel in air.

40. A siliceous material prepared using the method according to claim 1.

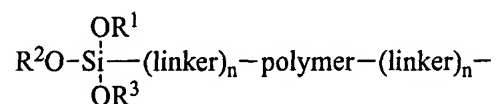
41. A method of preparing monolithic silica materials comprising combining an organic polyol silane precursor with one or more additives selected from water-soluble polymers and compounds of Formula I:



wherein R^4 is group selected from polymer-(linker)_n- and

$\begin{array}{c} \text{OR}^1 \\ | \\ \text{R}^2\text{O-Si-} \\ | \\ \text{OR}^3 \end{array} \text{-(linker)}_n\text{-polymer-(linker)}_n\text{-}$, under conditions where a phase transition occurs before gelation.

42. The method according to claim 41, wherein R^4 is



43. The method according to claim 42, wherein the linker group is a C₁₋₄alkylene group and n is 1.

44. The method according to claim 42, wherein OR¹, OR² and OR³ are the same and are selected from C₁₋₄alkoxy.

45. The method according to claim 42, wherein the polymer is PEO.

46. The method according to claim 41 wherein the compound of Formula I is selected from the group consisting of:

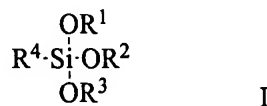
(CH₂CH₂O)_p[(EtO)₃Si(C₃H₆)]₂, p ~4-5, average MW 200 (Compound 5a);

$(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 13$, average MW 600 (Compound **5b**);
 $(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 44$, average MW 2000 (Compound **5c**); and
 $(\text{CH}_2\text{CH}_2\text{O})_p[(\text{EtO})_3\text{Si}(\text{C}_3\text{H}_6)]_2$, $p \sim 227$, average MW 10,000 (Compound **5d**).

47. The method according to claim 41, wherein the water soluble polymer is selected from the group consisting of PEO, PEO-NH₂ and poly(NIPAM).

48. A bimodal meso/macroporous silica monolith prepared using the method according to claim 41.

49. A method of preparing siliceous materials comprising combining an organic polyol silane precursor, a biomolecule of interest and an additive under conditions suitable for the hydrolysis and condensation of the precursor to a siliceous material, wherein the additive is selected from the group consisting of one or more water-soluble polymers and one or more trifunctional silanes of Formula I:



wherein R¹, R² and R³ are the same or different and represent a group that may be hydrolyzed under normal sol-gel conditions to provide a Si-OH group; and R⁴ is group that is not hydrolyzed under normal sol-gel conditions.

50. A siliceous material comprising a biomolecule entrapped therein wherein the siliceous material is prepared using the methods according to claim 49.

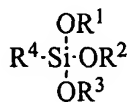
51. A method for the quantitative or qualitative detection of a test substance that reacts with or whose reaction is catalyzed by an active biological substance, wherein said biological substance is encapsulated within a siliceous material, comprising:

- (a) preparing the siliceous material comprising said active biological substance entrapped within a porous, silica matrix using a method according to claim 49;
- (b) bringing said biological-substance-containing siliceous material into contact with a gas or aqueous solution comprising the test substance; and
- (c) quantitatively or qualitatively detecting, observing or measuring the change in one or more characteristics in the biological substance entrapped within the siliceous material or, alternatively, quantitatively or qualitatively detecting, observing or measuring the change in one or more characteristics in the test substance.

52. The method according to claim 51, wherein the change in one or more characteristics of the entrapped biological substance is qualitatively or quantitatively measured by spectroscopy, utilizing one or more techniques selected from the group consisting of UV, IR, visible light, fluorescence, luminescence, absorption, emission, excitation and reflection.

53. A method of storing a biologically active biological substance in a silica matrix, wherein the biological substance is an active protein or active protein fragment, wherein the silica matrix prepared using a method according to claim 49.

54. A method of preparing a monolithic silica chromatographic column comprising placing a solution comprising an organic polyol silane precursor and one or more additives selected from water-soluble polymers and a compound of Formula I:



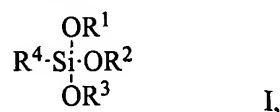
I,

wherein R^4 is group selected from polymer-(linker)_n- and

$$\begin{array}{c} \text{OR}^1 \\ | \\ \text{R}^2\text{O}-\text{Si}-(\text{linker})_n-\text{polymer}-(\text{linker})_n- \\ | \\ \text{OR}^3 \end{array}$$
, in a column under conditions suitable for a phase transition to occur before gelation.

55. The method according to claim 54, wherein the solution further comprises one or more substances, which provide cationic sites that counterbalance the anionic charge of the silica to reduce non-selective interactions

56. A chromatographic column comprising a silica monolith prepared by combining an organic polyol silane precursor and one or more additives selected from water-soluble polymers and a compound of Formula I:

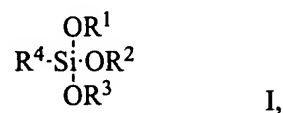


wherein R^4 is group selected from polymer-(linker)_n- and

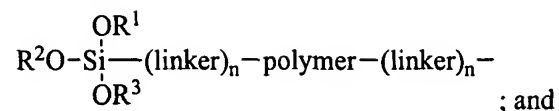
$$\begin{array}{c} \text{OR}^1 \\ | \\ \text{R}^2\text{O}-\text{Si}-(\text{linker})_n-\text{polymer}-(\text{linker})_n- \\ | \\ \text{OR}^3 \end{array}$$
, under conditions where a phase transition occurs before gelation.

57. A method of preparing a monolithic silica column having an active biomolecule entrapped therein comprising combining:

- a polyol-silane derived silica precursor;
- one or more additives selected from water soluble polymers and a compound of Formula I:



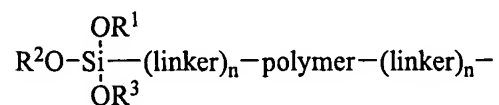
wherein R^4 is group selected from polymer-(linker)_n- and



c) a biomolecule;

under conditions wherein a phase separation occurs before gelation.

58. The method according to claim 57, wherein the additive is one or more water soluble polymers or a compound of Formula I, wherein R^4 is



59. The method according to claim 57, wherein the organic polyol silane silica precursor, one or more additives and biomolecule are also combined with a substance which provides cationic sites that counterbalance the anionic charge of the silica to reduce non-selective interactions, for example, aminopropyltriethoxysilane (APTES), PAM, PPG-NH₂ and PEG-NH₂.

60. A chromatographic column prepared using a method according to claim 57.

61. A use of the column according to claim 59, in methods for immunoaffinity chromatography, sample cleanup, solid phase extraction or preconcentration of analytes, removal of unwanted contaminants (for example by antibody binding), solid phase catalysis and frontal affinity chromatography (with or without mass spectral detection).